III.B.8 Effects of Sulfur and Polynuclear Aromatics on Catalytic Fuel Reforming

Objectives

- Investigate the effects of sulfur present in diesel fuel on reforming properties.
- Examine the role of support as well as metal catalyst in carbon formation for reforming reactions.
- Study the effects of polynuclear aromatics on reforming properties.

Accomplishments

- Investigated three different catalysts (Rh/$Ce_{0.56}Zr_{0.44}O_2$, Pt/$Ce_{0.56}Zr_{0.44}O_2$) to understand the role of support as well as metal catalyst in carbon formation in the presence of sulfur and aromatics.
- Studied the effects of sulfur on catalytic fuel reforming by introducing a hydrocarbon feed containing 50 ppm or 1,000 ppm sulfur in the form of dibenzothiophene.
- Examined the effects of polynuclear aromatics on reforming properties by feeding a 5 wt% 1-methylnaphthalene containing hydrocarbon feed to the reactor.
- Catalyst recovery after sulfur as well as polynuclear aromatics removal was also assessed for three catalysts studied.

Introduction

The U.S. Department of Energy is sponsoring development of high-temperature fuel cell power systems based on solid oxide technology through its Solid State Energy Conversion Alliance program. The program is geared at mass manufacturing of fuel cells for high volume markets and multiple applications. One of those markets/applications is a diesel-fueled auxiliary power unit for long-haul truck transportation. The fuel processor is a critical component of this system and must be able to provide a clean, tailored synthesis

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gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are also several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode. This, coupled with the high aromatic content present in diesel-like fuels, decreases the rate of reforming of other fuel components, such as paraffins, because the aromatics are strongly adsorbed to the active metal active sites. Therefore, it is particularly important to develop a catalyst which is stable and active for the reforming of diesel-like fuels into a hydrogen-rich gas for transportation as well as military applications.

Recently, the use of oxygen-conducting catalyst supports have garnered increasing interest due to their higher resistance to carbon formation, particularly for methane reforming [1-3], and resistance to sulfur poisoning as compared to traditional alumina-based supports. A recent review [4] shows that the rate of carbon deposition on nominally similar catalysts (primarily Ni-based) varies by several orders of magnitude, depending on the support. Ceria and zirconia were found to be effective, with a mixed ceria-zirconia support being superior to either in one case [5]. A temperature-dependent mechanism is postulated involving dissociative adsorption of oxygen on the metal and spillover to the support [6]. However, it is not clear if this mechanism would be applicable under conditions present in the reforming of liquid fuels [7].

In this study, the relationship between catalyst support, metal type, and deactivation was studied for three catalysts (Rh/$Ce_{0.56}Zr_{0.44}O_2$, Pt/$Ce_{0.56}Zr_{0.44}O_2$, and Pt/Al_2O_3) in a fixed bed catalytic reactor using a mixture of n-tetradecane (TD) and dibenzothiophene (DBT) or 1-methylnaphthalene (MN) to simulate diesel-like fuels. Reforming tests were conducted with TD to establish a baseline performance, while DBT (50 or 1,000 ppmw) or MN (5 wt% of feed) was added and removed throughout the test to observe their effect on reforming performance. A comparison of these three catalyst configuration is presented.

Approach

TD was used as a model diesel fuel compound to screen catalysts for activity and selectivity. The sulfur

tolerance of the catalysts was assessed through partial oxidation of TD containing 50 or 1,000 ppmw sulfur as DBT. MN (5 wt% of feed) was used as a model compound for polynuclear aromatics present in diesel fuel. These experiments were carried out by first running TD for one hour. Then, TD with 50 or 1,000 ppmw sulfur as DBT or 5 wt% MN was introduced as a step function and run for two hours. The samples were then switched back to the feed containing only TD to examine recovery. Catalyst tests were carried out in a fixed bed continuous-flow reactor. Nitrogen and air feed gases were delivered by mass flow controllers and the liquid feed was delivered by a high accuracy HPLC pump. Experiments were conducted at an O/C = 1.2, a GHSV = 50,000 h^{-1}, and 850°C. The catalyst was diluted with 5/1 quartz sand-to-catalyst ratio (by weight) to avoid preferential gas flow paths and hot spots.

The gases (N_2, O_2, CO, CO_2, and CH_4) were analyzed using a Thermo Onix mass spectrometer. The gaseous hydrocarbon products (C_1-C_6 paraffins, C_2-C_6 olefins, and benzene) were analyzed using a HP5890 gas chromatograph equipped with a flame ionization detector. Yield of product A (H_2, CO, and CO_2) is defined as:

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced} \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

Where, N is the number of moles of hydrogen per mole of hydrocarbon for H_2 yield and is the number of carbons in hydrocarbon fuel for yields of other products. The conversion of hydrocarbons is defined as:

$$\text{Conv (\%)} = \frac{(CO + CO_2 + \sum_{i}^{i=1-7} iC_iH_r) \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

Three catalysts used in this study were 1 wt% Pt/γ-Al$_2$O$_3$ (SA 198 m^2/g), 1 wt% Pt/ Ce$_{0.56}$Zr$_{0.44}$O$_{2-x}$, (SA 70 m^2/g), and Rh/Ce$_{0.56}$Zr$_{0.44}$O$_{2-x}$ (SA 69 m^2/g). Zirconia-doped ceria (ZDC), Ce$_{0.56}$Zr$_{0.44}$O$_{2-x}$, for the Pt and Rh catalysts were prepared by NexTech Materials (Worthington, OH) using a proprietary hydrothermal method. Oxygen-ion conductivity of ZDC material at 800°C was 4.3 mS/cm. Additional catalytic characterization such as x-ray diffraction (XRD), ion conductivity, and temperature programmed reduction can be found in a different publication [8]. Pt/γ-Al$_2$O$_3$ was used as a baseline catalyst and compared with Pt/ Ce$_{0.56}$Zr$_{0.44}$O$_{2-x}$ to see the effect of support on the reforming properties in the presence of sulfur. Pt/ZDC and Rh/ZDC were used to study the effect of metal catalyst on the reforming properties in the presence of sulfur.

Temperature programmed oxidation (TPO) of the spent catalyst was used to determine the amount of carbon formed during reforming reactions.
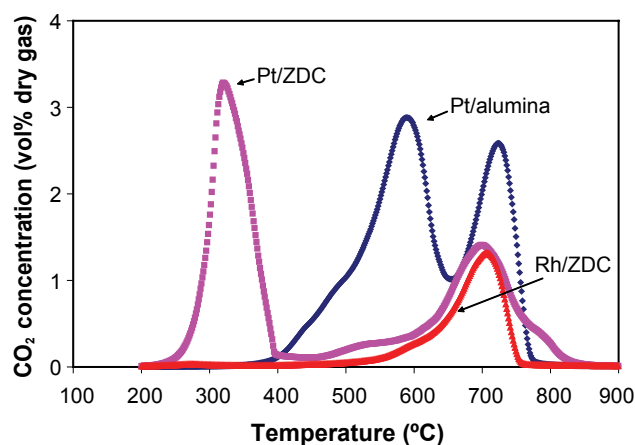
Results

Catalytic partial oxidation (CPOX) of n-tetradecane

Yields of H_2, CO, CO_2, and unsaturates (olefins + benzene); TD conversion; and amount of carbon formed for three catalysts are given in Table 1. All three catalysts studied showed very stable behavior during CPOX of TD for 5 hours. TD conversion to gaseous products was always more than 95%. Pt-based catalysts formed a significant amount of unsaturates and, thus, produced a higher amount of carbon compared to Rh/ZDC (no olefins or benzene formed from Rh/ZDC (see Table 1).

TABLE 1. Yields of H_2, CO, CO_2, and Unsaturates; TD Conversion; and Amount of Carbon Formed from Three Catalysts Studied

	Equilibrium	Pt/Al$_2$O$_3$	Pt/ZDC	Rh/ZDC
H$_2$ yield (%)	87	81	70	81
CO yield (%)	89	81	73	84
CO$_2$ yield (%)	10	17	20	15
Unsaturates yield (%)	0	0.8	1.5	0.0
Conversion (%)	100	>99	97	>99
Amount of carbon formed (g/g of catalyst)	0	0.85	0.69	0.21

A significant difference observed between these three catalysts was the formation of unsaturates, which are known coke precursors [9]. No unsaturates were observed from CPOX of TD only feed over the Rh/ZDC, whereas a significant amount of unsaturates was formed from Pt-based catalysts. The TPO of carbon deposited on the three catalysts studied is shown in Figure 1. It is obvious from Table 1 and Figure 1 that the amount of carbon deposited on the catalyst during CPOX reforming was directly related to unsaturates formation. The Rh/ZDC catalyst produced the least amount of carbon whereas Pt/alumina produced the highest amount of carbon, as expected from unsaturates formation on these catalysts. The ZDC-supported catalysts yielded a lower amount of carbon compared to the alumina-supported catalyst, most likely due to their oxygen-ion conductivity properties. The high oxygen-ion conductivity of oxygen-ion conducting supports such as ZDC may increase the rate of oxidation of adsorbed carbon species by reactive oxygen species [3]. Consequently, lower carbon deposition on the catalyst surface is observed from reforming reactions over oxygen-ion conducting supported metal catalysts.
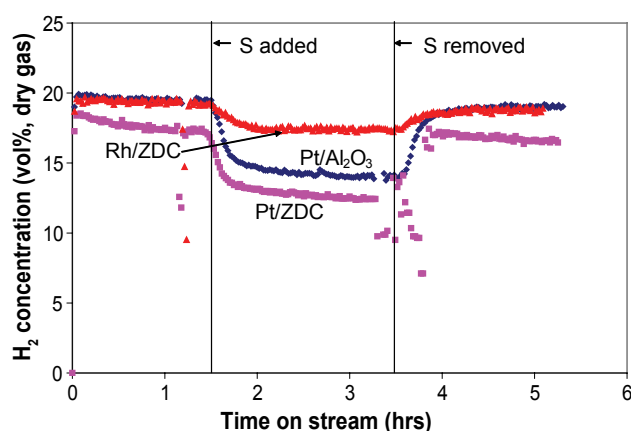
FIGURE 1. TPO of Carbon Deposited Catalysts

FIGURE 2. Step Response Plot for H_2 Production from TD with 50 ppmw Sulfur

FIGURE 3. Step Response Plot for CO Production from TD with 50 ppmw Sulfur

Two peaks were observed in the TPOs of the Pt-based catalysts as shown in Figure 1. The low temperature peak can be assigned to carbon deposition on metal sites [10] which can be gasified easily at low temperatures because metal catalyzes the carbon gasification. The low temperature peak on Pt/ZDC appeared at a much lower temperature than Pt/alumina – likely due to metal support interactions or different kinds of carbon formation on metal supported on oxide-ion conducting supports. The high temperature peak comes from the carbon deposited on the support. Interestingly, the high temperature peaks of all three catalysts appear at about 700°C, suggesting that this carbon is qualitatively similar for all these catalysts–and is assigned to the carbon deposited on the support. Both ZDC-supported catalysts showed almost similar peaks. However, there is undoubtedly more carbon of this type on the alumina than on the ZDC, which is certainly due to the oxygen-conducting properties of the ZDC. Furthermore, the TPO of used Rh/ZDC catalysts showed only a single peak at 700°C, suggesting that no carbon is formed on the Rh catalyst at the condition studied.

The nature of the metal catalyst also plays an important role in partial oxidation reactions of higher hydrocarbons. Rhodium supported on an oxygen-ion conductive material showed higher activity and lower carbon formation than platinum supported on the same.

CPOX of n-tetradecane in the presence of sulfur

The effects of 50 ppm sulfur as DBT in the feed on H_2 and CO production are shown in Figures 2 and 3, respectively, for all catalysts studied. The concentrations stabilized after 30 minutes online. H_2 and CO concentrations dropped upon introducing 50 ppmw sulfur in the feed for all three catalysts studied. However, the decline in H_2 and CO concentrations was more drastic for the Pt-based catalysts compared to
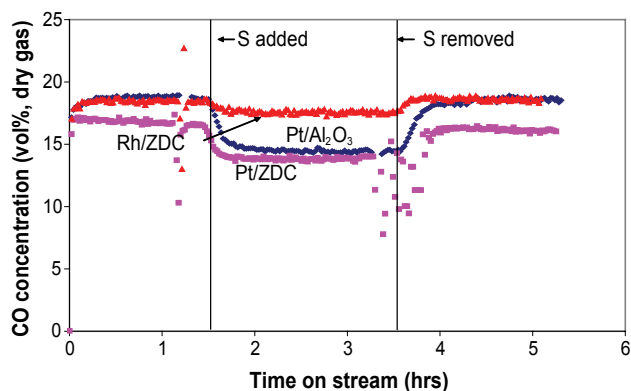
Rh/ZDC. For the Rh catalyst, H_2 and CO concentrations dropped from 20 and 19 vol%, before the step DBT input, to 18 and 18 vol% respectively, after the introduction of DBT. Furthermore, H_2 concentrations continued to decline after introduction of DBT for the Pt-based catalysts while H_2 concentrations dropped to a near-stationary level for the Rh catalysts. Interestingly, CO concentrations dropped to a stationary level after introduction of DBT for all three catalysts studied, suggesting preferential poisoning of the sites responsible for H_2 formation.

However, the higher concentrations (1,000 ppmw) of sulfur significantly affect the performance, particularly of Pt-based catalysts (Figures 4 and 5). By introducing 1,000 ppmw sulfur in the feed, the drop in H_2 concentrations was considerable over time compared to CO or CO_2 concentrations. The H_2/CO ratio before sulfur introduction was >1, while it became <1 (<0.5 for Pt-based catalysts) after sulfur introduction. Also, selectivity to unsaturates increased as selectivity to
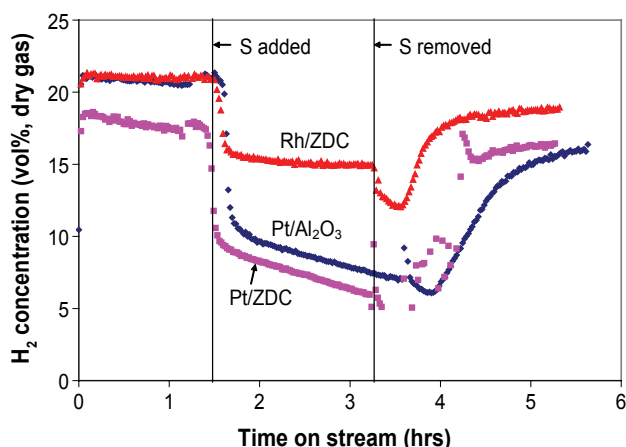
FIGURE 4. Step Response Plot for H_2 Production from TD with 1,000 ppmw Sulfur
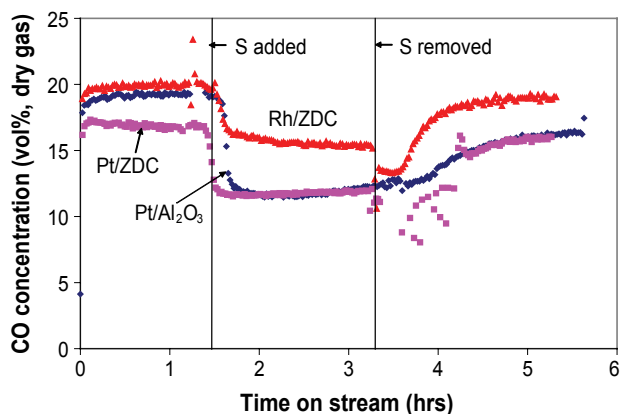
FIGURE 5. Step Response Plot for CO Production from TD with 1,000 ppmw Sulfur

syngas decreased. This was more significant for the Pt-based catalysts, suggesting more gas phase chemistry occurs when the catalyst is deactivated. Consequently, more carbon formation was observed during the reforming of a sulfur-containing feed (Table 2). TD conversion decreased to 70-80% (depending on the catalyst) in the presence of sulfur.

TABLE 2. Amount of Carbon Formed (g/g of catalyst)

	TD	TD + 50 ppm S	TD + 1,000 ppm S	TD + 5% MN
Pt/Al$_2$O$_3$	0.85	0.92	2.44	2.88
Pt/ZDC	0.69	-	1.46	1.45
Rh/ZDC	0.21	0.56	0.95	0.89

Catalyst activity was nearly restored for H_2 and CO after removing the sulfur from the feed for the ZDC-based catalysts, but not for the Pt/alumina catalyst,

which only partially recovered. Catalyst activity recovery after sulfur removal from the feed for Rh/ZDC and Pt/ZDC suggests that the sulfur is weakly adsorbed on the surface of those catalysts so it can be removed easily afterwards. It was not clear whether sulfur causes deactivation directly by sulfur poisoning or indirectly by excessive carbon formation. However, this kind of catalytic activity drop can be overcome by decreasing the space velocity (to balance the less available surface caused by occupied sulfur) or increasing the temperature to weaken the sulfur-metal interactions.

CPOX of n-tetradecane in the presence of 5 wt% MN

Effects of 5 wt% MN in the feed on reforming activities were similar to 1,000 ppmw sulfur in the feed. H_2 and CO concentrations dropped upon introducing 5 wt% MN in the feed, less significantly for Rh/ZDC compared to Pt-based catalysts. For the Rh catalyst, H_2 and CO concentrations dropped from 21 and 20 vol%, before the step MN input, to 16 and 17 vol% respectively, after the introduction of MN. Similar to sulfur results, H_2 concentrations declined continuously over time after introduction of MN for the Pt-based catalysts while H_2 concentrations dropped to a stationary level for the Rh catalysts. CO concentrations dropped to a stationary level after introduction of MN for all three catalysts studied. Also, by introducing aromatics in the feed, the drop in H_2 concentrations was considerable over time compared to CO or CO_2 concentrations. The H_2/CO ratio before MN introduction was >1, while it became <1 (<0.5 for Pt-based catalysts) after MN introduction. However, catalyst activity was almost completely restored for H_2 and CO after removing the MN from the feed for the Rh/ZDC, but not for the Pt-based catalysts, which only partially recovered. More carbon formation was observed during the reforming of a MN containing feed compared to reforming of TD only feed. Also, hydrocarbon conversion decreased to 70-80% (depending on the catalyst) in the presence of aromatic compound in feed.

Conclusions and Future Directions

- The effects of 1,000 ppmw sulfur and 5 wt% 1-MN in the CPOX of TD include decreased H_2 and CO yields, kinetic inhibition, and reversible deactivation.
- The activity was partially restored after removing the sulfur or aromatics from the feed.
- The Rh/ZDC catalyst showed less kinetic inhibition than either Pt/ZDC or Pt/Al$_2$O$_3$.
- The higher oxygen-ion conductivity of the ZDC support appears to improve the resistance to carbon formation in the CPOX of TD.
- Sulfur effects are very catalyst sensitive.

- Rate of carbon formation increased with S in the feed.
- GHSV has to be adjusted to accommodate a decrease in kinetics due to the presence of aromatics or sulfur in the feed.

FY 2006 Publications/Presentations

1. D. Shekhawat, T. H. Gardner, D. A. Berry, J. J. Spivey, Catalytic Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Applications, *Catalysis,* Royal Society of Chemistry, Cambridge, UK, Vol. 19, Chapter 6, 184-253.

2. D. Shekhawat, D. A. Berry, T. H. Gardner, M. Salazar, D. J. Haynes, J. J. Spivey, Support Effects for Pt and Rh-Based Catalysts for Partial Oxidation of n-Tetradecane, *Applied Catalysis A: General*, (in press).

3. D. Shekhawat, T. H. Gardner, D. A. Berry, Fuel Constituent Effects on Fuel Reforming Properties for Fuel Cell Applications, *231st ACS National Meeting*, Mar 26-30, 2006, Atlanta, GA.

4. D. Shekhawat, D. A. Berry, T. H. Gardner, D. J. Haynes, J. J. Spivey, T. Xiao, M. L. H. Green, Partial Oxidation Reforming of n-Tetradecane over Pt and Carbide Catalysts: A Comparative Study, *231st ACS National Meeting*, Mar 26-30, 2006, Atlanta, GA.

5. D. A. Berry, D. Shekhawat, T. H. Gardner, M. Salazar, D. J. Haynes, J. J. Spivey, Support Effects for Pt and Rh-Based Catalysts for Partial Oxidation of n-Tetradecane, *The Fourth International Conference on Fuel Cell Science, Engineering and Technology*, Jun 19-21, 2006, Irvine, CA.

6. D. Shekhawat, D. A. Berry, T. H. Gardner, Diesel Fuel Reforming Studies, 2006 NETL Fuel Reforming Annual Merit Review.

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